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(54) Acrylic Modified Reactive Urethane Hot Melt Adhesive Compositions

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ABSTRACT

The addition to urethane prepolymers of low molecular weight polymers formed from ethylenically unsaturated monomers which do not contain active hydrogen provides a hot melt adhesive which can be readily coated at a viscosity of 3000 to 50,000 cps. at 120°C Thermosel without the need for additional tackifiers or plasticizers and which has improved initial cohesive strength as well as improved strength after aging of the cured bond. In a preferred embodiment of the invention, the ethylenically unsaturated monomers are polymerized in the non-isocyanate containing components of the isocyanate terminated prepolymer.

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ACRYLIC MODIFIED REACTIVE URETHANE HOT MELT ADHESIVE COMPOSITIONS

Background Of The Invention

The present invention is directed to low viscosity reactive urethane hot melt adhesive compositions which are improved with respect to their cohesive and adhesive strength by the addition thereto of low molecular weight acrylic resins. In accordance with one embodiment of the invention, the acrylic monomer(s) is polymerized in the non-isocyanate component of the polyurethane prepolymer and the latter then reacted with suitable isocyanate functionalities to form a hot melt adhesive composition having a suitable coating viscosity without the necessity for addition of plasticizers or tackifiers.

Hot melt adhesives are 100% solid materials which do not contain or require any solvents. They are solid materials at room temperature but, on application of heat, melt to a liquid or fluid state in which form they are applied to a substrate. On cooling, the adhesive regains its solid form and gains its cohesive strength. In this regard, hot melt adhesives differ from other types of adhesives which achieve the solid state through evaporation or removal of solvents or by polymerization.

In order to obtain the required physical properties, most hot melt adhesives are formulated from thermoplastic materials which are applied molten at elevated temperatures and bond rapidly on cooling. Unfortunately, their thermoplastic nature also results in a bond which is heat sensitive and which may fail where the bond is subjected to even moderate heat.

Hot melt adhesive compositions which are applied in molten form, cool to solidify and subsequently cure by a chemical crosslinking reaction have been prepared using specific thermosetting materials such as polyurethanes. These hot melts exhibit superior heat resistance but have little inherent strength and resemble a heavy balsam or grease prior to undergoing cross-linking. In addition, these polyurethane based hot melt adhesives lack adequate adhesion to many commercial substrates such as polyvinyl chloride film, Mylar* and aluminum. Attempts have been made to improve the initial adhesive strength of polyurethane hot melts by the addition of certain thermoplastic resins as taught, for example, in U.S. Pat. No. 3,931,077 issued Jan. 6, 1976 to Uchigaki et al. These thermoplastic resins are, however, generally high molecular weight (i.e., greater than about 100,000) materials so their addition appreciably raises the coating viscosity of the adhesive requiring the further addition of plasticizers or tackifiers in order to sufficiently reduce the viscosity so as to facilitate its application. While lowering the hot viscosity of the formulated adhesive, the addition of these plasticizing and tackifying components, in the relatively large amounts required, has a detrimental effect upon the adhesive properties of the polyurethane hot melt, particularly after aging of the bond.

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It is therefore an object of the present invention to provide an improved polyurethane hot melt adhesive composition characterized by superior initial adhesion to an unusually broad range of substrates as well as heat resistance even after aging of the bonds.

Summary of the Invention

We have found that the addition of urethane prepolymers to low molecular weight polymers formed from ethylenically unsaturated monomers which do not contain active hydrogen, provides hot melt adhesives which are solid at room temperature and which can be readily coated at a viscosity of 3000 to 50,000 cps at 120°C Thermosel without the need for additional tackifiers or plasticizers and which have improved initial cohesive strength as well as improved strength after aging of the cured bond. Moreover, the adhesives exhibit these improved properties on a wide range of substrates including difficult to bond substrates such as polyvinyl chloride, Mylar (polyester film from DuPont) and aluminum.

The low molecular weight polymer may be added to the polyol prior to reaction with the isocyanate components or it may be added to the already formed prepolymer. The products of this invention may also be formed through the simultaneous polymerization of the urethane prepolymer and the ethylenically unsaturated monomers. The polyurethane prepolymer may also be polymerized in the ethylenically unsaturated monomers, which are then subsequently polymerized to form the product of the invention. Alternatively, the ethylenically unsaturated monomers may be polymerized in the polyol using free radical polymerization procedures. In this embodiment, the isocyanate components are subsequently polymerized with the mixture using conventional condensation polymerization procedures. This latter polymerization procedure has the advantage of excellent control of the molecular weight of the resulting vinyl polymer (as determined by

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intrinsic viscosity) and also produces a polymer which is free of detrimental impurities. In addition, the reduction in the handling and inventory of materials and elimination of intermediate packaging and storage bring about significant cost savings.

Detailed Description of The Preferred Embodiments

Any ethylenically unsaturated monomer capable of free radical polymerization and which does not contain active hydrogen may be used herein. Most commonly employed are the C_1 to C_{12} esters of acrylic and methacrylic acids including, but not limited to methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, n-propyl or iso-propyl acrylate as well as the corresponding methacrylates. Mixtures of compatible (meth)acrylate monomers may also be used. Such mixtures, including mixtures of butyl and methyl methacrylate are well known in the art. Additional ethylenically unsaturated monomers such as vinyl esters (e.g., vinyl acetate and vinyl propionate), vinyl ethers, fumarates, maleates, styrene, acrylonitrile, ethylene, vinyl ethers, etc. may be used as may copolymers thereof. The choice of the particular monomer(s) is largely dependent upon the desired end use of the adhesives. For example, one skilled in the art would recognize that selection of certain monomers will produce a pressure sensitive adhesive, while other monomers will give a non-pressure sensitive material. Similarly, appropriate monomers may be selected to formulate structural adhesives, conductive adhesives, etc.

The urethane prepolymers are those conventionally used in the production of polyurethane hot melt adhesive compositions. In general, the prepolymer is prepared by the condensation polymerization of a polyisocyanate with a polyol, preferably the polymerization of a diisocyanate with a diol. The polyols used include polyhydroxy ethers (substituted or unsubstituted polyalkylene ether glycols or polyhydroxy polyalkylene ethers), polyhydroxy polyesters, the ethylene or propylene oxide adducts of polyols and the mono-substituted esters of glycerol.

Any suitable organic polyisocyanate may be used such as, for example, ethylene diisocyanate, ethylidene diisocyanate, propylene diisocyanate, butylene diisocyanate, hexamethylene diisocyanate, toluene diisocyanate, cyclopentylene-1,3,-diisocyanate, cyclohexylene-1,4-diisocyanate, cyclohexylene-1,2-diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,2-diphenylpropane-4,4'- diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, xylylene diisocyanate, 1,4-naphthylene diisocyanate, 1,5-naphthylene diisocyanate, diphenyl-4,4'-diisocyanate, azobenzene-4,4'-diisocyanate, diphenylsulphone-4,4'-diisocyanate, dichlorohexamethylene diisocyanate, furfurylidene diisocyanate, 1-chlorobenzene-2,4-diisocyanate, 4,4',4"-triisocyanato-triphenylmethane, 1,3,5-triisocyanato-benzene, 2,4,6-triisocyanato-toluene, 4,4'-dimethyldiphenylmethane-2,2',5,5-tetraisocyanate, and the like.

The polyisocyanate and polyol components are combined in proportions so as to yield a urethane prepolymer characterized by an isocyanate content of from about 0.25 to about 15%, preferably to about 10%. In addition, the ratio of isocyanate equivalents to hydroxyl equivalents (known as the isocyanate index) should be greater than 1 but no more than about 2. By maintaining the low isocyanate index, we are able to reduce the level of free isocyanate content in the final hot melt adhesive composition to less than about 4%, preferably less than 1%. It will be recognized that the presence of higher levels of free isocyanate has a detrimental effect on a hot melt formulation since it causes toxic fumes to be released when the adhesive is heated to application temperature. The higher levels of free isocyanate may also cause reduction in viscosity and poorer initial bond strength of the adhesive. The precise amount of the polyisocyanate used in the polymerization will depend on the equivalent weight of the polyol, the amount of the polyol and the

particular polyisocyanate employed. In general, the amount of the polyisocyanate needed to achieve the isocyanate content will vary from about 5 to about 55% of the final prepolymer.

In accordance with the broadest scope of the invention, the ethylenically unsaturated monomer may be polymerized using conventional free radical polymerization procedures to a relatively low molecular weight. For purposes of clarification herein, by "low molecular weight" we mean weights in the range of approximately 10,000 to 30,000. The low molecular weight is obtained by careful monitoring and controlling the reaction conditions and, generally, by carrying out the reaction in the presence of a chain transfer agent such as dodecyl mercaptan. There is a recognized correlation between intrinsic viscosity and molecular weight and we have found that, in general, monomers polymerized to an intrinsic viscosity of 0.1 to 0.4 (I.V. as measured in a 9:1 mixture of tetrahydrofuran and alcohol) are particularly preferred for use herein. In this embodiment, the low molecular weight polymer is then blended either with the polyol and dissolved therein prior to reaction with the isocyanate component or the low molecular weight polymer is dissolved in the already formed urethane prepolymer. In either case, low molecular weight polymer is combined with the isocyanate terminated urethane prepolymer in a proportion such that the reactive curing hot melt adhesive contains about 5 to 90% of the urethane prepolymer and 95% to 10% of the low molecular weight polymer. Care should be taken in storing and handling the low molecular weight polymer to avoid contamination with ambient moisture or other factors which might affect the stability of the prepolymer system. The resultant hot melt adhesive may then be applied in

molten form to the substrate to be bonded using techniques known to those skilled in the art. The urethane hot melt cures over time with ambient moisture to form a crosslinked network.

In accordance with an alternate method for preparing the urethane prepolymers of the invention, the ethylenically unsaturated monomers are combined in an amount of about 2 to 90% by weight with 10 to 98% by weight of the polyol and polymerized therein using conventional free radical polymerization procedures in the presence of a chain transfer agent such as dodecyl mercaptan to achieve the low molecular weight polymer dissolved in the polyol. Subsequent to the polymerization of the ethylenically unsaturated monomer(s), the polyisocyanate and any additional ingredients required for the urethane prepolymer forming reaction are added and that reaction is carried out using conventional condensation polymerization procedures. In this manner, the resultant isocyanate terminated urethane prepolymer forms the reactive curing hot melt adhesive described above which contains about 5 to 90% of the urethane prepolymer and 95 to 10% of the low molecular weight polymer which may be applied in molten form to the substrate and cured over time with ambient moisture to form a crosslinked network.

It is also possible to polymerize the low molecular weight polymer in the presence of the already formed isocyanate terminated urethane prepolymer. This method has the drawback of subjecting the prepolymer to unnecessary heating during the acrylic polymerization, heating that might result in branching, viscosity increase, depletion of needed isocyanate groups and possible gellation. Although these disadvantages are subject to control, more stringent control of conditions are required as compared to polymerization in the non-isocyanate functional urethane components. When the reaction is run

in the polyol or other non-isocyanate containing component, there is also the advantage of lower reaction viscosities and reduced exposure to isocyanate vapors because of the lesser amount of heating required.

As discussed previously, the resultant hot melt adhesives which are solid at room temperature have appropriate coating viscosities within the range of 3000 to 50,000 cps at 120°C Thermosel (which corresponds to about 1500 to 25,000 at 135°C and 10,000 at 108°C) and thus require no additional tackifiers and/or plasticizers in order to achieve these coating viscosities. It is noted, however, that small amounts of tackifiers or plasticizers may be added so long as their presence does not serve as a detriment to the desired adhesive properties.

Not only do the adhesives cure to form a strong heat resistant bond, they also exhibit high initial adhesive and cohesive strength so that the bonded structure, even before curing, can be readily handled and subjected to further processing operations. As such, they are readily adapted to a wide variety of applications for which hot melt adhesives are commonly used, especially those applications which require a high degree of heat resistance as might be encountered in processing or sterilizing operations including, but not limited to, laminating, bookbinding, labelling of bottles and pouches, automotive interior assembly, fabrication of non-woven products for metal uses, etc.

It is hypothesized that those superior properties are due, in part, to the formation of semi-interpenetrating and interpenetrating networks as well as, in some cases, the formation of graft copolymers. The semi-interpenetrating network would result when the urethane prepolymer (a thermoset) is used with a free radically polymerized polymer which contains no crosslinking groups (thermoplastic). When the free radically polymerized polymer contains crosslinking groups, a fully interpenetrating

network will result. Grafting occurs with certain types of urethane prepolymer components such as those containing a carbon atom bearing a tertiary hydrogen atom. Such tertiary hydrogen atoms are potential graft sites for the acrylic or vinyl monomers.

This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated. In the following examples, the polymeric reagents are characterized in terms of their weight-averaged molecular weights.

Example I

A one liter reaction vessel was set up equipped with a condenser, gas inlet tube, slow addition tube, thermometer, stirrer, and provisions for heating/cooling. The ingredients of the reaction consisted of the following:

1. Polypropylene glycol (1000 mol wt.)	275.8 gm
2. 1,6-hexane diol, neopentyl glycol adipate (3000 M.W.)	88.9 gm
3. 1,6-hexane diol, neopentyl glycol adipate (1000 M.W.)	29.3 gm
4. Butyl methacrylate	17.8 gm
5. Butyl methacrylate	94.1 gm
6. Methyl methacrylate	9.4 gm
7. Methyl methacrylate	53.6 gm
8. Dodecyl mercaptan	0.68 gm
9. Benzoyl peroxide	1.7 gm
10.Benzoyl peroxide	0.6 gm
11.Methylene bis phenyl diisocyanate	131.1 gm

The reaction vessel was purged with dry nitrogen and a slow stream of dry nitrogen was bubbled subsurface throughout the reaction. Ingredients designated 1, 2, 3, 4, 6, 8 and 9 were added to the vessel and the temperature raised to 80°C. After 1/2 hr at 80°C ingredients 5 and 7 were added uniformly over a period of 1 hr. The reaction was held at 80°C for an additional three hours, at which time 10 was added. The reaction was held an additional 2 hrs. @ 80°C and 11 was added; then the temperature

was raised to 100°C and held for three hours. At this point a vacuum of 120mm to 130mm was applied to the vessel for 20 minutes to 30 minutes and the reaction poured hot from the flask.

Properties:

% Methacrylate polymer	25%
Ratio of butyl methacrylate to methyl methacrylate	64 to 36
% Urethane prepolymer	75%
% isocyanate groups	1.9%
Viscosity at 100°C	64,000 cps
Viscosity at 120°C	25,250 cps
Viscosity at RT	Solid
Intrinsic Viscosity in tetrahydrofuran/ethanol=9/1	0.18
Color	water white to very slightly amber
Clarity	clear to very slightly hazy
Calculated urethane prepolymer mol. wt.	3315 mol. wt.
Isocyanate Index	1.6

Example II

An experiment was run as in Example I where the viscosity of the system was lowered by reducing the molecular weight of the urethane prepolymer as an alternative method to that of reducing the molecular weight of the methacrylate resin. All factors were the same except for the following:

Ingredients	A	B
Butyl methacrylate	18.0 gm	18.0 gm
Butyl methacrylate	102.0 gm	102.0 gm
Methyl methacrylate	10.1 gm	10.1 gm
Ingredients (cont'd)	A	B
Methyl methacrylate	57.4 gm	57.4 gm
Dodecyl mercaptan	0.63 gm	0.72 gm
Benzoyl peroxide	1.8 gm	1.8 gm
Methylene bis phenyldiisocyanate	168.6 gm	168.6 gm

The properties were:

Properties:	A	B
% Methacrylate polymer	25%	25%
Ratios of butyl methacrylate to methylmethacrylate	64 to 36	64 to 36
% Urethane prepolymer	75%	75%
% isocyanate groups	3.1%	3.3%
Viscosity at 100°C	53,000 cps	51,000 cps

Viscosity at 120°C	not measured	7,062 cps
Viscosity at room temperature	Solid	Solid
Intrinsic viscosity in THF/ETOH=9/1	0.18	0.15
Color	water white to very slightly amber	
Clarity	clear to very slightly hazy	
Calculated urethane prepolymer molecular weight	2032 mol. wt.	1909 mol. wt.
Isocyanate Index	2.0	2.0

Example III

This example discloses the preparation of a urethane prepolymer composed of a combination of 70% polypropylene glycol of molecular weight 1000 M.W. and 30% 1,6-hexane diol neopentyl glycol adipate diol of 2000 molecular weight with sufficient methylene bis phenyl diisocyanate to provide 2% NCO content in the prepolymer.

Ingredients:

Polypropylene glycol (1000 molecular weight)	350.0
1,6-hexane diol neopentyl glycol adipate diol (2000 mol. wt.)	150.0
Methylene bis phenyl diisocyanate	166.4

Procedure:

A one liter reaction vessel was equipped with a condenser, gas inlet tube, thermometer, stirrer, and provisions for heating and cooling. The reaction vessel was purged with dry nitrogen and a slow stream was bled through the vessel. The polyols were added to the vessel and the temperature was raised to 80°C. At this point, the diisocyanate was added and the reaction was heated to 100°C and held at that temperature for 4 hrs. After the 4 hr. heating period, the reaction was poured hot from the vessel.

The properties of the urethane prepolymer were:

Properties:

% isocyanate groups	2.3%
Viscosity at 100°C	3200 cps
Viscosity at room temperature	800,000 cps
Color	very slightly amber
Clarity	clear
Isocyanate Index	1.6

Example IV (Comparative)

This example is provided to illustrate the production of a hot melt adhesive according to U.S. Pat. No. 3,931,077 using a blend of a polyurethane prepolymer, a thermoplastic resin and a tackifier.

Prepolymer from Example III	60%
CRL 715* (a 35% n-butyl acrylate - 65% ethylene copolymer having a melt index of 70 from USI)	5%
PRL-300* (a terpene phenolic resin having a softening point of 108°C from Reichhold Chemical)	35%

The urethane prepolymer was placed in a three-neck flask and heated to 167°F under dry nitrogen gas, the two additional ingredients were added and stirred under nitrogen until dissolved. The adhesive was designated IVA.

A second hot melt adhesive (designated IVB) was formulated as above using 10 parts Exxon EX 170* (25% vinyl acetate, 75% ethylene with a melt index of 2400); 25 parts of the PRL-300* and 65 parts of the urethane prepolymer of Example III.

Testing

The following series of tests have been developed to characterize the adhesives of this invention and measure their effectiveness.

Tensile and elongation of cured free films: This test measures the strength of the film and its elasticity. The tensile strength and degree of elongation are related to a materials' utility as an adhesive. In

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general a material that possesses high tensile strength and appropriate elongation will show better adhesive performance than a material which is poor in one or both categories.

In this test, films were cast from the melt on a low energy surface at approx. 3-5 mils thickness. (Films in this range had to be used as heavier films developed excessive voids on curing.) The films were cured by exposing them to the atmosphere in a constant temperature room with 22°C and 50% R.H. for one week.

Adhesion Test: Samples where prepared using various flexible substrates by coating the substrate with 1.0 mil of molten adhesive and immediately laminating to a 3/8" particle board by subjecting the lamination to 10 minutes in a cold press at approx 5 psi. pressure. All samples were allowed 1 week to cure or crosslink. They were then subjected to a 90° peel test at a withdrawal rate of 12 inches per minute.

Heat Resistance: As most hot melts are thermoplastic and deform or flow when subjected to temperatures above 82°C., we have devised a series of shear tests at elevated temperatures, to measure resistance to flow or deformation at higher temperatures, up to 175°C.

In this test a lap shear of 5 mil bare aluminum foil to 3/8" particle board with an adhesive application of 1 mil is used. All samples were cured 1 week. The samples were placed in a circulating air oven at 108°C with a load of 1 kilogram per sq./inch. They were allowed to remain at this temperature for 15 min, then the temperature was elevated to 120°C and observed for 15 min. and then again the temperature was elevated at regular intervals until failure was observed.

Green Strength: This test measures the bond immediately after application and bonding. This is important as it tests the strength of the uncured, material prior to curing. Sufficient green strength must be present to

hold substrates together when combined, and while the cure develops with ambient moisture. Green strength or immediate bond strength prior to cure as well as rate of cure, is very important for the fabrication or lamination process prior to full cure.

In this test, the adhesive samples in molten condition at 120°C were coated at exactly 1.0 mil thickness on 2 mil Mylar film and immediately nipped to 5 mil aluminum foil. The resultant lamination of Mylar/Adhesive/Foil was then peeled immediately, and after the indicated times using an Instron tester at 12 inch/min.

Comparison of Viscosity at 120°C

Example	Visc. @ 120°C (Thermosel)*
I	11,625 cps
IIB	5,500 cps
III	1,138 cps
IVA	9,000 cps
IVB	5,000 cps

Comparison of Tensile/Elongation

Example	Ultimate Tensile	% Elongation
I	1,350 psi	460%
IIB	3,250 psi	440%
III	667 psi	440%
IVA	960 psi	520%
IVB	200 psi	1400%

Note low tensiles in III and IV, and the increased tensile with good elongation of I and II which are examples of this invention. Also note higher tensile in II which correlates with higher NCO content.

*Viscosity measurement using Brookfield Thermosel System TM.

Adhesion Test Results

	5 mil Bare Alum Foil	2 mil Mylar	6 mil Woodgrain Vinyl	4 mil Embossed White Vinyl
Example I	6.5 lbs^{FT}	4.2 lbs^{FT}	5.5 lbs^{FT}	4.5 lbs^{FT}
Example II A	5.5 lbs^{FT}	1.5 lbs	6.5 lbs^{FT}	5.5 lbs^{FT}
Example III	1.7 lbs	1.8 lbs	6.6 lbs^{FT}	5.2 lbs
Example IV A	7.6 lbs^{FT}	0.4 lbs	0.2 lbs	4.0 lbs^{FT}
Example IV B	6.7 lbs^{FT}	0.9 lbs	7.0 lbs^{FT}	4.5 lbs^{FT}

FT = fiber tear

Examples I and II both gave excellent bonds to most substrates and Example I gave excellent adhesion to all substrates including Mylar. Note failure was FT (fiber tear). The adhesive carried with it the top fibers of the particle board substrate. Example II lacked adhesion only to Mylar. Example III lacked adhesion to foil and Mylar; Example IVA to Mylar and vinyl and Example IVB to Mylar.

Comparison of Heat Resistance

Example	108°C	120°C	134°C	150°C	162°C	175°C
I	OK	OK	OK	OK	13 minutes to fail	—
II (A & B)	OK	OK	OK	OK	OK	8 hours
III	OK	OK	OK	9 minute to fail	—	—
IV A	1 minute to fail	—	—	—	—	—

Comparison of Heat Resistance (cont'd)

Example	108°C	120°C	134°C	150°C	162°C	175°C
IV B	1 minute to fail	—	—	—	—	—

This test illustrates the poor heat resistance of Examples IVA and IVB (examples of the prior art) and the superior heat resistance of Example I and II, with Example II the high NCO type, giving the best heat resistance.

Comparison of Bond Strength

	Example I	Example II(A)	Example III	Example IVA	Example IVB
Immediate (green)	300 gms	170 gms	20 gms	120 gms	2100 gms
1 hour	375 gms	170 gms	25 gms	205 gms	1800 gms
2 hours	375 gms	172 gms	65 gms	206 gms	1850 gms
3 hours	363 gms	180 gms	125 gms	375 gms	1800 gms
24 hours	1200 gms	680 gms	700 gms	425 gms	1900 gms
48 hours	1200 gms	N/T	N/T	272 gms	908 gms
1 week	1500 gms	N/T	N/T	91 gms	771 gms

N/T = Not Tested

The above test results clearly indicate the superior properties of the hot melts of the present invention over the prepolymer with no acrylic added and also over the material covered in US 3,931,077, with respect to bond strength and heat resistance particularly after aging.

The following examples incorporate modifications of our most preferred embodiment so as to illustrate various aspects of the invention.

Example V

The procedure of Example I was repeated except that 0.8 gm dodecyl mercaptan was used instead of 0.68 gm. This change was made to reduce the molecular weight (as indicated by a lower intrinsic viscosity) of the methacrylate copolymer portion of the product and thus reduce the viscosity of the product.

The properties were:

Properties:

% Methacrylate polymer	25%
Ratio of butyl methacrylate to methyl methacrylate	64 to 36
% Urethane prepolymer	75%
% isocyanate groups	2.0%
Viscosity at 100°C	18,000 cps

Viscosity at room temperature	Solid
Intrinsic viscosity in tetrahydrofuran/ethanol=9/1	0.15
Color	water white to very slightly amber
Clarity	clear to very slightly hazy
Isocyanate Index	1.6

Example VI

An experiment was run as in Example I except that the docedyl mercaptan chain transfer agent was decreased to 0.54 gm in order to increase the molecular weight of the methacrylate polymer and thus increase the viscosity as compared to Example II.

The properties were:

Properties:

% Methacrylate polymer	25%
Ratio of butyl methacrylate to methyl methacrylate	64 to 36
% Urethane prepolymer	75%
% isocyanate groups	3.0%
Viscosity at 100°C	72,000 cps
Viscosity at 120°C	16,250 cps
Viscosity at room temp.	Solid
Intrinsic viscosity in THF/ETOH=9/1	0.15
Color	water white to very slightly amber
Clarity	clear to very slightly hazy
Isocyanate Index	1.6

Example VII

The following example represents a variation of Example I in the following significant areas:

1) Change in ratio of methacrylate polymer to urethane prepolymer from 25/75 to 30/70.

2) Change in ratio of butylmethacrylate to methyl methacrylate from 64/36 to 80/20.

3) Change in composition of the urethane prepolymer from polypropylene glycol/1,6-hexane diol, neopentyl glycol adipate-methylene bis phenyl diisocyanate to polypropylene glycol-methylene bis phenyl diisocyanate.

This example was run as in Example I except that the following amounts were used.

Ingredients

Polypropylene glycol (1000 mol wt.)	300.3
Butyl methacrylate	23.0
Butyl methacrylate	130.6
Methyl methacrylate	5.8
Methyl methacrylate	32.6
Dodecyl mercaptan	0.3 gm
Benzoyl peroxide	1.9 gm
Benzoyl peroxide	0.6 gm
Methylene bis phenyl diisocyanate	147.8 gm

The properties were:

Properties:

% Methacrylate polymer	30.0%
Ratio of butyl methacrylate to methyl methacrylate	80 to 20
% urethane prepolymer	70.0%
% isocyanate groups	3.9%
Viscosity at 100°C	104,000 cps
Viscosity at room temperature	Solid
Intrinsic viscosity in THF/ETOH=9/1	0.19
Color	water white
Clarity	clear to very slightly hazy
Isocyanate Index	2.0

Example VIII

The following example illustrates the use of a different acrylate monomer. The example was run as in Example I but with the ingredients as noted below.

Ingredients:

Polypropylene glycol (mol. wt. 1000)	326.4 gm
Butyl acrylate	150.0 gm
Dodecyl mercaptan	0.3 gm
Benzoyl peroxide	2.0 gm
Methylene bis phenyl diisocyanate	122.8 gm

Properties:

% Acrylate polymer	25.0%
% Urethane prepolymer	75.0%
% isocyanate groups	1.7%
Viscosity at 100°C	7200 cps
Viscosity at room temperature	$>2.8 \times 10^6$
Intrinsic viscosity in THF/ETOH=9/1	0.15
Color	lt. brown

Clarity	opaque
Isocyanate Index	1.5

Example IX

In this example, an isocyanate other than methylene bis phenyl diisocyanate was used. The example was run as in Example I but with the ingredients noted below.

Formula	gm.
Polypropylene glycol (1000 mol. wt.)	275.7
1,6-hexane diol, neopentyl adipate diol (2000 mol. wt.)	118.2
Butyl methacrylate	17.8
Butyl methacrylate	94.1
Methyl methacrylate	9.1
Methyl methacrylate	53.6
Dodecyl mercaptan	0.68
Benzoyl peroxide	1.7
Benzoyl peroxide	0.6
Methylene bis cyclohexyl diisocyanate	137.4
Dibutyl tin dilaurate	0.08

Properties:

% Methacrylate polymer	25%
Ratio of butyl methacrylate to methyl methacrylate	64-36
% Urethane prepolymer	75%
% Isocyanate groups	2.2%
Viscosity at 120°C.	5000 cps (est)
Viscosity at RT	Solid
Intrinsic Viscosity in tetrahydrofuran/ethanol = 9/1	.13
Color	Water White
Clarity	Clear
Isocyanate Index	1.6

Example X

In this example, a catalyst was added to accelerate the cure speed. Again, the reaction was run using the procedure of Example I.

Formula	gm.
Polypropylene glycol (1000 mol. wt.)	275.7
1,6-hexane diol, neopentyl adipate diol (2000 mol. wt.)	118.2
Butyl methacrylate	17.8
Butyl methacrylate	94.1
Methyl methacrylate	9.4
Methyl methacrylate	53.6
Dodecyl mercaptan	0.68

Benzoyl peroxide	1.7
Benzoyl peroxide	0.6
Methylene bis phenyl diisocyanate	131.1
Dibutyl tin dilaurate	0.30

Properties:

% Methacrylate polymer	25%
Ratio of butyl methacrylate to methyl methacrylate	64 to 36
% Urethane prepolymer	75%
% Isocyanate groups	1.9%
Viscosity at 100°C.	84,000 cps
Viscosity at RT	Solid
Intrinsic Viscosity in tetrahydrofuran/ethanol =9/1.	.17
Color	Water White to Very Slightly Amber
Clarity	Clear to Very Slightly Hazy
Isocyanate Index	1.6

Example XI

In this example, the procedure of Example I was repeated with the acrylate comonomers replaced by styrene. The ingredients and properties follow.

Ingredients:	gm.
Polypropylene glycol (1000 mol. wt.)	275.7
1,6-hexane diol, neopentyl adipate diol (2000 mol. wt.)	118.2
Styrene	174.9
Dodecyl mercaptan	0.68
Benzoyl peroxide	1.7
Benzoyl peroxide	0.6
Methylene bis phenyl diisocyanate	131.1

Properties:

% Styrene polymer	25%
% Urethane prepolymer	75%
% Isocyanate groups	1.7
Viscosity at RT	Solid
Intrinsic Viscosity in tetrahydrofuran/ethanol =9/1	0.23
Color	Sl. Yellow
Clarity	Cloudy
Isocyanate Index	1.6

Example XII

Again, the procedures of Example I was repeated with the acrylate copolymer replaced by vinyl acetate. The ingredients and properties follow.

Ingredients:	gm.
Polypropylene glycol (1000 mol. wt.)	275.7
1,6-hexane diol, neopentyl adipate diol (2000 mol. wt.)	118.2
Vinyl acetate	174.9
Dodecyl mercaptan	0.68
Benzoyl peroxide	1.7
Benzoyl peroxide	0.6
Methylene bis phenyl diisocyanate	137.4

Properties:	
% Vinyl acetate polymer	25%
% Urethane prepolymer	75%
% Isocyanate groups	2.0
Viscosity at 121°C	1800 cps
Viscosity at RT	>4 x 10^6 cps
Intrinsic Viscosity in tetrahydrofuran/ethanol = 9/1	0.15
Color	Sl. Amber
Clarity	Cloudy
Isocyanate Index	1.6

Example XIII

This example illustrates the addition of a commercially available low molecular weight polymer to the urethane prepolymer to produce a hot melt adhesive in accordance with an alternate embodiment of the present invention. Elvacite 2013* is a 64% butylmethacrylate/36% methylmethacrylate copolymer of I.V. 0.2 available from DuPont. The Elvacite* was vacuum dried in a dessicator for 24 hours immediately prior to use herein.

Ingredients:	
Polypropylene Glycol (1000 Mol. wt.)	472.9 gm
1,6-hexanediol neopentyl glycol adipate (2000 Mol. wt.)	202.7
Elvacite 2013	300.0
Methylene bisphenyl diisocyanate	224.9

* Trade Mark

Procedure:

The polyols and the Elvacite 2013 were added to the vessel and heated to 100°C until the Elvacite was dissolved. At that point the methylene bisphenyl diisocyanate was added, and the reaction was held at 100°C for 3 hrs. After the 3 hours at 100°C the reaction was poured hot from the vessel. The samples had the following properties:

Properties

% Methylacrylate polymer	25%
% Urethane prepolymer	75%
% Isocyanate groups	2.0%
Viscosity at 100°C	86,000 cps
Viscosity at 120°C	8,000 cps
Viscosity at room temp.	Solid
Intrinsic viscosity in 9:1 THF/EtOH	0.25
Color	water white
Clarity	clear to very slightly hazy
Isocyanate Index	1.6

Test Results

Ultimate Tensile Strength	1700 psi
% Elongation	400%
Viscosity Stability at 120°C:	
initial	8,000 cps
after 8 hours	12,125 cps
Bond Strength (foil/mylar):	
immediate	908 gms
1 hour	1025 gms
2 hours	1040 gms
3 hours	1100 gms
24 hours	1750 gms
Adhesion test (90°C peel):	
Mylar	1.7 lbs.
5 ml foil	5.5 lbs.
Woodgrain vinyl	6.9 lbs. FT
white vinyl	5.7 lbs. FT

Heat Resistance (2 psi):

180°C	OK
120°C	OK
134°C	OK
150°C	OK
162°C	10 minutes to failure

EXAMPLE XIV

For the purposes of comparison of initial (green) strength properties, additional adhesives (designated 1-4) were prepared according to the invention using the procedures discussed previously. Five other adhesives were prepared following Examples II, III, IV, V and IX, (respectively designated 5-9), of U.S. Patent No. 3,968,089 to Cuscurida et al.

The components and amounts (in grams) of raw materials utilized are shown in Table I.

The intrinsic viscosities, isocyanate index and viscosity and room temperature were determined and are shown in Table II.

TABLE II

Adhesive	Intrinsic Viscosity (I.V.) in 9:1 THF/EtOH	Isocyanate Index (1.1)	Viscosity at Room Temp (CPS) Pa
1	0.11	1.9	Solid
2	0.18	1.6	Solid
3	0.15	1.6	Solid
4	0.17	1.6	Solid
5	0.09	12.9	74,000
6	0.09	12.0	17,440
7	0.07	16.5	1,960
8	0.09	21.1	1,520
9	0.09	13.1	31,000

The following test procedures were used to determine the initial (green) strength performance of the adhesives. Results of the testing are shown in Table III.

Peel Test Wood-grained vinyl substrate was coated with 1.0-1.5 mil thickness of adhesive heated @ approx. 120°C (direct or transfer) and pressed together with 3/8" thickness particle board 3-5 sec in a press @ 5

lbs. The sample was peeled at 90° in a peel tester e.g. Instron Tester at rate of 5"/min. (Sample dimension = 1/2" width strip, 3-4" length). The sample was peeled immediately from press i.e., within 1-2 minutes.

Lap Shear Five mil. gauge aluminim was coated with 2-3 mil. thickness of adhesive heated at approx. 120°C (direct or transfer). The coated aluminum was pressed together with 3/8" thickness particle board 3-5 sec. in a press at approx. 5 lbs. The sample was pulled at 180° in a tensile tester (e.g. Instron Tester) at rate of 0.2 inches per minute. (Sample dimension 1/2" X 1/2" bond area.) The sample was pulled immediately from press i.e., within 1-2 minutes.

TABLE III

Adhesive	Peel (lbs./in.)	Lap Shear (lbs./in.)
1	4.2-4.4	31.5
2	4.0-4.0	18.2
3	1.0-1.1	9.3
4	1.4-1.7	15.1
5	No Initial Bond	No Initial Bond
6	No Initial Bond	No Initial Bond
7	No Initial Bond	No Initial Bond
8	No Initial Bond	No Initial Bond
9	No Initial Bond	No Initial Bond

It will be apparent that various changes and modifications may be made in the embodiments of the invention described above, without departing from the scope of the invention, as defined in the appended claims, and it is intended therefore, that all matter contained in the foregoing description shall be interpreted as illustrative only and not as limitative of the invention.

TABLE I

Adhesive	Isocyanate	Amt.	Polyols: Polyester	Amt.	Polyols: Polyether	Amt.	Resin or Monomers	Amt.
1[A]	Methylene Bis Phenyl Diisocyanate	84.0	1,6-Hexane Diol Neopentyl Glycol Adipate 2000 MW*	350.0	—		Ethylmethyl-acrylate Copolymer	144.7
2[B]	Methylene Bis Phenyl Diisocyanate	112.5	1,6-Hexane Diol Neopentyl Glycol Adipate 2000 MW	101.4	Polypropylene Glycol 1000 MW	236.5	Methyl/butyl Methacrylate Copolymer	150.0
3[B]	Methylene Bis Phenyl Diisocyanate	133.7	1,6-Hexane Diol Neopentyl Glycol Adipate 2000 MW	118.2	Polypropylene Glycol 1000 MW	275.7	Methyl Methacrylate Butyl Methacrylate	63.0 111.9
4[D]	Methylene Bis Phenyl Diisocyanate	133.7	1,6-Hexane Diol Neopentyl Glycol Adipate 2000 MW	118.2	Polypropylene Glycol 1000 MW	275.7	Methyl Methacrylate Butyl Methacrylate	63.0 111.9
5	Polymethylene Polyphenyl Polyisocyanate	199.8	—	—	Polyethylene Polypropylene Triol 5500 MW	200.0	Styrene Acrylonitrile	15.0 15.0
6	Polymethylene Polyphenyl Polyisocyanate	225.0	—	—	Polyethylene Polypropylene Triol 5500 MW	225.0	Styrene Acrylonitrile	25.0 25.0
7	Isophorone Diisocyanate	450.0			Polyethylene Polypropylene Triol 5500 MW	450.0	Styrene Acrylonitrile	50.0 50.0

* Trade Mark

TABLE I (cont'd)

Adhesive	Isocyanate	Amt.	Polyols: Polyester	Amt.	Polyether	Amt.	Monomers	Amt
8	Toluene Diisocyanate	450.0	—	—	Polyethylene Polypropylene Triol 5500 MW	450.0	Styrene Acrylonitrile	50. 50.
9	Polymethylene Polyphenyl Polyisocyanate	450.0	—	—	Polyethylene Polypropylene Diol 4000 MW	450.0	Styrene Acrylonitrile	50. 50.

(A) Procedure of Example XIII
(B) A repeat of Example XIII
(C) Similiar to Example I
(D) Resin polymerized in prepolymer using 1.4 grams benzoyl peroxide, 3.5 grams azobisisobutyronitrile, and 1.4 gram acetyl peroxide as initiator and 0.68 grams dodecyl mercaptan as a chain transfer agent.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A solvent-free hot melt polyurethane adhesive composition which is solid at room temperature consisting essentially of:

(a) 5 to 90% by weight of a urethane prepolymer having an isocyanate content of 0.25 to 15% and an isocyanate index greater than 1 and no more than about 2;

(b) 10 to 95% by weight of a low molecular weight polymer of ethylenically unsaturated monomers containing no active hydrogen, the monomers being polymerized to an intrinsic viscosity of 0.1 to 0.4 as measured in a 9:1 mixture of tetrahydrofuran and alcohol; said hot melt adhesive formulation being characterized, in the absence of tackifiers or plasticizers, by a viscosity of 3000 to 50,000 cps at 120°C (Thermosel).

2. The hot melt adhesive composition of claim 1 wherein the ethylenically unsaturated monomer is selected from the group consisting of C_1 to C_{12} esters of acrylic and methacrylic acid, vinyl esters and ethers, fumarates, maleates, styrene, acrylonitrile, ethylene and mixtures thereof.

3. The hot melt adhesive composition of claim 1 wherein the urethane prepolymer is prepared from the condensation polymerization of a polyol and a polyisocyanate.

4. The hot melt adhesive composition of claim 1 wherein the urethane prepolymer is prepared from the condensation polymerization of a diol and a diisocyanate.

5. The hot melt adhesive composition of claim 3 wherein the polyol is selected from the group consisting of substituted or unsubstituted polyalkylene ether glycols or polyhydroxy polyalkylene ethers, polyhydroxy polyesters, the ethylene or propylene oxide adducts of polyols and the mono-substituted esters of glycerol.

6. The hot melt adhesive composition of claim 1 wherein the polyisocyanate is selected from the group consisting of ethylene diisocyanate, ethylidene diisocyanate, propylene diisocyanate, butylene diisocyanate, hexamethylene diisocyanate, toluene diisocyanate, cyclopentylene-1,3-diisocyanate, cyclohexylene-1,4-diisocyanate, cyclohexylene-1,2-diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,2-diphenylpropane-4,4'-diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, xylylene diisocyanate, 1,4-naphthylene diisocyanate, 1,5-naphthylene diisocyanate, diphenyl-4,4'-diisocyanate, azobenzene-4,4'-diisocyanate, diphenylsulphone-4,4'-diisocyanate, dichlorohexamethylene diisocyanate, furfurylidene disocyanate, 1-chlorobenzene-2,4-diisocyanate, 4,4',4"-triisocyanato-triphenylmethane, 1,3,5-triisocyanato-benzene, 2,4,6-triisocyanato-toluene and 4,4'-dimethyldiphenylmethane-2,2',5,5-tetraisocyanate.

7. The hot melt adhesive composition of claim 1 wherein the free isocyanate content is 0.25 to 4%.

8. The hot melt adhesive composition of claim 7 wherein the free isocyanate content is less than 1%.

9. A solvent-free hot melt adhesive polyurethane composition which is solid at room temperature consisting essentially of an isocyanate terminated polyurethane prepolymer containing polymerized therein a low molecular weight polymer of an ethylenically unsaturated monomer wherein the isocyanate terminated polyurethane prepolymer has an isocyanate content of from 0.25 to 15% and an isocyanate index greater than 1 and no more than about 2; said adhesive prepared by the steps of:

(1) combining 2 to 90% by weight of an ethylenically unsaturated monomer containing no active hydrogen and 10 to 98% by weight of a polyol;

(2) polymerizing the mixture of (1) by free radical polymerization with chain transfer agents to achieve a low molecular weight polymer having an intrinsic viscosity of 0.1 to 0.4 as measured in a 9:1 mixture of tetrahydrofuran and alcohol;

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(3) adding thereto sufficient polyisocyanate to yield the desired isocyanate content and isocyanate index and polymerizing by condensation polymerization.

10. The hot melt adhesive composition of claim 9 wherein the ethylenically unsaturated monomer is selected from the group consisting of C_1 to C_{12} esters of acrylic and methacrylic acid, vinyl esters and ethers, fumarates, maleates, styrene, acrylonitrile, ethylene and mixtures thereof.

11. The hot melt adhesive composition of claim 8 wherein the urethane prepolymer is prepared from the condensation polymerization of a diol and a diisocyanate.

12. The hot melt adhesive composition of claim 9 wherein the polyol is selected from the group consisting of substituted or unsubstituted polyalkylene ether glycols or polyhydroxy polyalkylene ethers, polyhydroxy polyesters, the ethylene or propylene oxide adducts of polyols and the mono-substituted esters of glycerol.

13. The hot melt adhesive composition of claim 9 wherein the polyisocyanate is selected from the group consisting of ethylene diisocyanate, ethylidene diisocyanate, propylene diisocyanate, butylene diisocyanate, hexamethylene diisocyanate, toluene diisocyanate, cyclopentylene-1,3-diisocyanate, cyclohexylene-1,4-diisocyanate, cyclohexylene-1,2-diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,2-diphenylpropane-4,4'-diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, xylylene diisocyanate, 1,4-naphthylene diisocyanate, 1,5-naphthylene diisocyanate, diphenyl-4,4'-diisocyanate, azobenzene-4,4'-diisocyanate, diphenylsulphone-4,4'-diisocyanate, dichlorohexamethylene diisocyanate, furfurylidene disocyanate, 1-chlorobenzene-2,4-diisocyanate, 4,4',4"-triisocyanato-triphenylmethane, 1,3,5-triisocyanato-benzene, 2,4,6-triisocyanato-toluene and 4,4'-dimethyldiphenylmethane-2,2',5,5-tetraisocyanate.

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14. The hot melt adhesive composition of claim 9 wherein the free isocyanate content is 0.25 to 4%.

15. The hot melt adhesive composition of claim 14 wherein the free isocyanate content is less than 1%.

16. A solvent-free hot melt polyurethane adhesive composition which is solid at room temperature consisting essentially of:

(a) 5 to 90% by weight of a urethane prepolymer having an isocyanate content of 0.25 to 15% and an isocyanate index greater than 1 and no more than about 2;

(b) 10 to 95% by weight of a low molecular weight polymer of ethylenically unsaturated monomers containing at least one moisture reactive functional group but no active hydrogen, the monomers being polymerized to an intrinsic viscosity of 0.1 to 0.4 as measured in a 9:1 mixture of tetrahydrofuran and alcohol; said hot melt adhesive formulation being characterized, in the absence of tackifiers or plasticizers, by a viscosity of 3000 to 50,000 cps at 120°C (Thermosel).

17. A process for the production of a solvent-free hot melt polyurethane adhesive composition which is solid at room temperature characterized, in the absence of added tackifiers or plasticizers, by a viscosity of 3000 to 50,000 cps at 120°C (Thermosel), comprising the steps of:

(1) combining 2 to 90% by weight of an ethylenically unsaturated monomer containing no active hydrogen and 10 to 98% by weight of a polyol;

(2) polymerizing the mixture of (1) by free radical polymerization with chain transfer agents to achieve a low molecular weight polymer having an intrinsic viscosity of 0.1 to 0.4 as measured in a 9:1 mixture of tetrahydrofuran and alcohol;

(3) adding thereto sufficient polyisocyanate to yield an isocyanate content of 0.25 to 15% and an isocyanate index greater than 1 and less than about 2 and polymerizing by condensation polymerization.

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18. A process for the production of a solvent-free hot melt polyurethane adhesive composition which is solid at room temperature characterized, in the absence of added tackifiers or plasticizers, by a viscosity of 3000 to 50,000 cps at 120°C, comprising the step of polymerizing, to a low molecular weight by free radical polymerization to an intrinsic viscosity of 0.1 to 0.4 as measured in a 9:1 mixture of tetrahydrofuran and alcohol in a urethane prepolymer having an isocyanate content of 0.25 to 15% and an isocyanate index greater than 1 and no more that about 2, at least one ethylenically unsaturated monomer containing no active hydrogen; in a ratio such that the final product contains 5 to 90% by weight of the urethane prepolymer and 0 to 95% by weight of the low molecular weight polymer.

19. A process for the production of a solvent-free hot melt polyurethane adhesive composition which is solid at room temperature characterized, in the absence of added tackifiers or plasticizers, by a viscosity of 3000 to 50,000 cps at 120°C (Thermosel), comprising the steps of:

(1) dissolving a low molecular weight polymer of ethylenically unsaturated monomers containing no active hydrogen and having an intrinsic viscosity of 0.1 to 0.4 as measured in a 9:1 mixture of tetrahydrofuran and alcohol in the non-isocyanate urethane prepolymer component and

(2) forming the urethane prepolymer by reacting the mixture of (1) with a polyisocyanate in an amount sufficient to provide an isocyanate index greater than 1 and no more than about 2 and in a ratio such that the final product contains 5 to 90% by weight of the urethane prepolymer and 0 to 95% by weight of the low molecular weight polymer.

20. A process for the production of a solvent-free hot melt polyurethane adhesive composition which is solid at room temperature characterized, in the absence of added tackifiers or plasticizers, by a viscosity of 3000 to 50,000 cps at 120°C (Thermosel), comprising the step of dissolving a low molecular weight polymer of ethylenically unsaturated monomers containing no active hydrogen in a urethane prepolymer and having an intrinsic viscosity of 0.1 to

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0.4 as measured in a 9:1 mixture of tetrahydrofuran and alcohol, having an isocyanate content of 0.25 to 15% and an isocyanate index greater than 1 and no more than about 2; in a ratio such that the final product contains 5 to 90% by weight of the urethane prepolymer and 0 to 95% by weight of the low molecular weight polymer.